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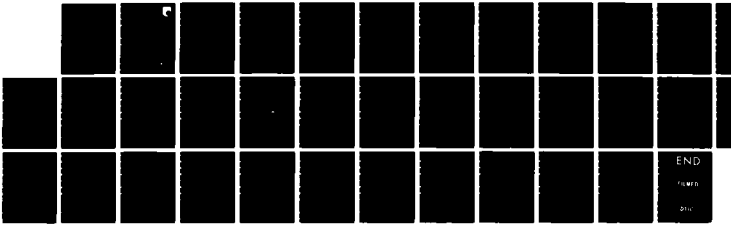

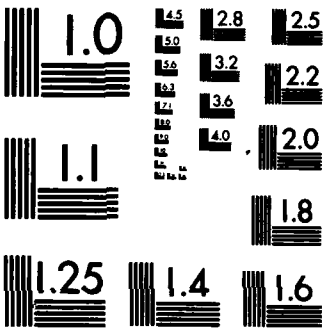

AFWAL-TR-85-1035

COMPOUND SEMICONDUCTOR INSULATOR INTERFACE RESEARCH

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Final Report for Period July 1981 - January 1985

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A second phase of the program was devoted to theory. This work was done with additional support from ONR Contract N00014-79-C-0133. We achieved significant progress in two areas; developing ways of treating the vibrational properties of insulators, and ways of treating defect states in non-orstalline insulating and semiconducting materials.

The major accomplishments of the program are (ii) the development of a low temperature deposition process for making stoichiometric films of both Si_3N_4 and SiO_2; (ii) the development of a model for the chemistry in this deposition process; (iii) the development of a trilayer gate insulator for (In, Ga)As IGFET's; (iv) the development of a theory for the vibrational properties of glassy insulators that includes specifically the intermediate range order; and (v) the development of theoretical techniques for treating the properties of native bonding defects in noncrystalline solids.

EXECUTIVE SUMMARY

This is the final report for Air Force Contract F33615-81-C-1428. It covers the time period from 1 July 1981 through 2 January 1985. Work under this contract has been performed in two departments at North Carolina State University, the Departments of Physics and Chemistry. The major thrust of the research program has been in the area of semiconductor/insulator interfaces with the emphasis on the development of materials that could be used for gate insulators in Insulated Gate Field Effect Transistor Devices (IGFET's). To achieve this goal, we collaborated with the research group at the Research Triangle Institute (RTI),(with additional support under NAVELEC Contract N00039-81-C-0661), and targeted our research efforts to the development of a gate insulator for (In,Ga)As IGFET's. We have designed and built a low temperature CVD deposition system, and developed a process, using Remote Plasma Enhanced CVD (RPECVD), for depositing a multilayer dielectric consisting of Si_3N_4 and SiO_2 layers onto (In,Ga)As. We have have determined the conditions necessary to achieve stoichiometry in each of the constituent layers. We have also determined the deposition conditions which minimize the incorporation of defect and impurity atom bonding groups. We have developed a model for the deposition process which can serve as a guideline for deposition of other silicon based insulators, e.g., SiN_xF_y and SiO_xF_y alloys.

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A. INTRODUCTION

The research is directed to the question of semiconductor/insulator interfaces, with particular emphasis on the development of insulating materials that can be utilized in device configurations for III-V compound semiconductor field effect transistors. There has been considerable interest in the use of deposited insulators for use in IGFET devices, but there has been very little success in fabricated stable, high gain device structures [1]. There are two different sets of problems which can limit success in this area; these are (1) the quality of the semiconductor surface, and (2) the quality of the deposited insulators. Technology for III-V semiconductors cannot be based on a grown native insulator that parallels the growth of SiO_2 layers on c-Si. The oxides in general are not homogeneous, and oxidation is known to lead to phase separation and/or preferential oxidation of one of the atomic constituents of the III-V material [2]. III-V surfaces are subject to chemical degradation when raised to elevated temperatures, simply due to the fact that the individual atomic components generally have very different partial pressures. These considerations mandate a low temperature process for a non-native insulator.

After a review of the literature, we had decided to pursue a plasma enhanced CVD approach that included the removal of the substrate from the plasma region. The approach chosen has been designated by us as Remote Plasma Enhanced CVD (RPECVD), and consists of a process wherein one gas phase component is plasma excited to generate either atoms, or excited molecules or radicals. These are then transported to another region of the deposition chamber and reacted with a neutral molecular species. This reaction yields a gas phase precursor which in turn undergoes a low temperature (200-300^{o}C) CVD reaction at the semiconductor surface. We have grown films of Si_3N_4 by reacting excited N_2 or NH_3 with neutral SiH_4, and films of SiO_2 by reacting excited O_2 with neutral SiH_4. We have used a variety of chemical techniques, including IR, XPS, AES and RBS to determine compound stoichiometry and impurity content (to the 0.5 atomic

percent regime). We have analyzed the properties of Si_3N_4 and SiO_2 layers deposited on p-type (In,Ga)As FET structures, and have found that neither layer by itself makes an acceptalbe device component. However, the use of a dielectric trilayer structure, SiO_2-Si_3N_4-SiO_2, has yielded high gain (75 mS/mm), stable (less that 5 percent drift in 24 hours of DC bias) devices.

We have also been successful in extending the theory of insulating glasses in two distinct areas: the vibrational properties of glassy insulators including intermediate range order, and the electronic properties of native bonding defects and impurity atoms in non-crystalline insulators and semiconductors. Both techniques are based on Bethe Lattice representations of the structure.

B. OBJECTIVES OF THE RESEARCH PROGRAM

The objectives are the research program were essentially five in number:

1. To design and construct a system for the low temperature deposition of thin insulating films of Si_3N_4, SiO_2 and other dielectrics.
2. To deposit insulating films of suitable quality for use as gate insulators in III-V IGFET devices, and to characterize their chemical and electrical properties.
3. To study the insulating films in device structures employing III-V semiconductor FET configurations.
4. To perform theoretical studies of the vibrational and electronic properties of non-crystalline materials.

All of the objectives stated above were met during the three and one half year period of this contract. The next section highlights the specific accomplishments relative to each of these objectives, and the following section goes into a more detailed technical discussion of our activities and the progress that we have made.

C. MAJOR ACCOMPLISHMENTS

This section will be organized according to the identification of objectives that are given above. We will therefore discuss the accomplishments under four subheadings that follow below.

1. Design and Construction of Deposition System

We have constructed and operated a system for low temperature deposition of dielectric thin films. The base pressure attained in the system prior to deposition is less than 5×10^{-8} Torr. The system can be baked out to remove residual gases from the chamber walls. The system is designed to handle up to twelve different gases. Six can enter through the excitation region, and six through a gas dispersal ring. The details of the system design are given in the technical discussion section.

2. Deposition of Insulating Films of Si_3N_4 and SiO_2

We have deposited near stoichiometric films of Si_3N_4 by two different reactions that are given below:

$(NH_3)^* + SiH_4 \text{ -----> } Si_3N_4$, and

$(N_2)^* + SiH_4 \text{ -----> } Si_3N_4$.

In each instance the films are free of oxygen and SiH groups (detection limit about 0.5 atomic percent). The films do however contain evidence for NH groups.

We have deposited near stoichiometric films of SiO_2 by the reaction given below:

$(O_2,He)^* + SiH_4 \text{ -----> } SiO_2$.

In this case the films are free of nitrogen and SiH groups (detection limit about 0.5 atomic percent). The films show very small amounts of OH contamination, less than 1 atomic percent.

3. Device Configurations

In collaboration with the group at RTI, we have studied the use of the dielectric layers of Si_3N_4 and SiO_2 as gate insulators for (In,Ga)As IGFET's. We have developed a trilayer configuration, consisting of a SiO_2 (100 A)-Si_3N_4 (600 A)-SiO_2 (100 A) sandwich, that has performed quite well as a gate insulator. The trilayer was deposited on p-type layers of (In,Ga)As (grown on InP). For devices with a channel width of 3 microns and a channel length of 250 microns, transconductances up to 75 mS/mm were achieved. Devices showed drift of less than 5 percent for DC bias voltages applied for period of 24 hours. The device showed surface inversion with conduction taking place in an n-channel in the "on" state.

4. Theory

We have explored two basic questions in the theory on non-crystalline solids: (1) the vibrational properties of glassy insulators, including for the first time the effects on intermediate range order, and (2) the effects of near neighbor chemistry on the energies of native bonding defects in non-crystalline semiconductors and insulators. We have calculated the vibrational density of states, and the IR and Raman response of glassy insulators using a Bethe Lattice technique that included configurational averaging over a restricted basis set of dihedral angles. These calculations have clearly identified the role played by intermediate range order (IRO) in oxide glasses. We have shown that the energies of dangling bond, and "wrong" bond defects in the gap can be perturbed by near-by chemical impurities in the non-crystalline network. This represents the first calculations of induction effects on localized electronic states.

D. TECHNICAL DISCUSSION

This section of the report is organized in five sections: (1) the deposition system; (2) the deposition process chemistry; (3) characterization of deposited insulators; (4) device fabriacation and performance; and (5) theory-(a) vibrational properties of glassy insulators and (b) defect states in non-crystalline materials.

1. The Deposition System

Figure 1 shows a schematic presentation of the deposition system. The design and operation of the system are most easily specified in terms of five subsystems we now list: (a) the high vacuum pumping system; (b) the process pump and scrubbing system; (c) the gas handling system; (d) the deposition chamber; and (e) the control system.

a. The High Vacuum System

The system employs a turbomolecular pump to achieve a base pressure of less than 5×10^{-8} Torr in the sample chamber. The system can be baked out in order to remove residual gases from the walls of the chamber, primarily water vapor. Once the system is brought to its base pressure, the turbomolecular pump is isolated from the system via a gate valve, and all subsequent pumping is done via the process pumping system.

b. The Process Pump and Scrubbing System

This consists of a roots blower backed up by a rotary vane pump. This system maintains a process vacuum level between 100 and 500 mTorr for gas flow rates of the order of 10 to 200 sccm. All gases withdrawn through the system are passed through a water scrubber system being exhausted to the atmosphere via a dedicated exhaust line. The scrubber in the system is one that we have designed and built at NCSU. We had orginally used a commercial scrubber, but this system failed, with a crack developing at a cold joint in the apparatus. The newly designed and constructed system is built of PVC with all joints being glued. Connections

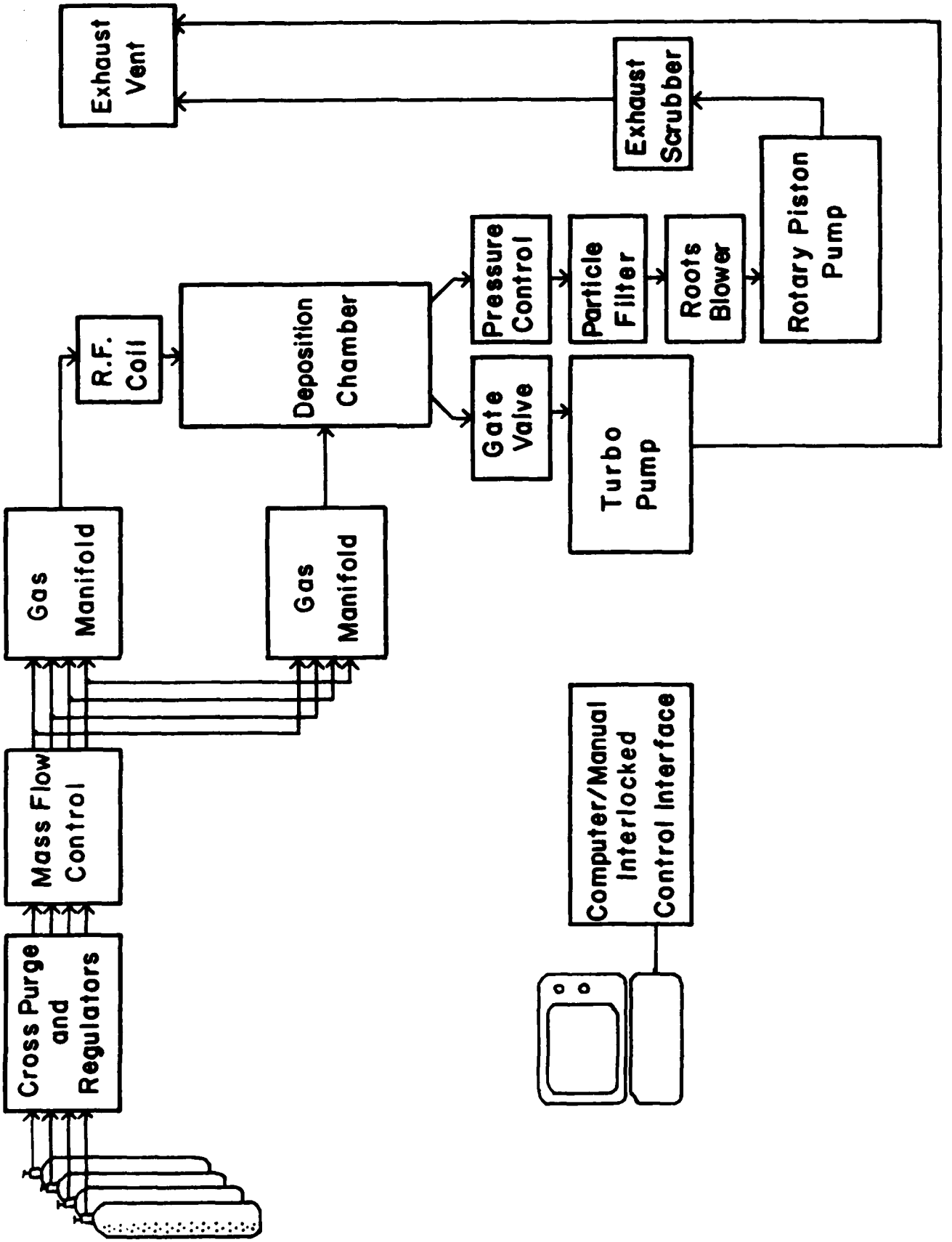

Figure 1 - Schematic Representation of Deposition System

between the scrubber and the pumping system are made through flexible PVC pipe to minimize vibrations.

c. The Gas Handling System

Process gasses are introduced into the reaction chamber in two ways: (1) through the top of the chamber, where there is provision of inductive excitation via a 13.6 MHz RF power source, and (2) through a gas dispersal ring (see Fig. 2). We have twelve mass flow controllers and a gas delivery system so that any one of six different lines can feed either of the two gas delivery ports. Gas flow rates can be varied from approximately 0.1 t0 200 sccm. Up to 500 W of RF power are available for excitation.

d. The Reaction Chamber

The heart of our system is the reaction chamber shown in Fig. 2. As noted above gases can be delivered into the system from two different positions in the chamber. Process gas can be inductively excited in the glass section of the delivery tube at the top of the chamber and then introduced into the main chamber. This is the port through which the excited species (indicated by the * notation) are introduced, either $(NH_3)^*$, $(N_2)^*$ or $(O_2,He)^*$. Table I gives flow rates of these gases used in the process for deposited stoichiometric layers of either Si_3N_4 or SiO_2. Neutral silane (SiH_4) diluted with N_2 is introduced through the gas dispersal ring. The ring is located five cm below the top of the chamber and five cm above the substrate. The substrate holder can accommodate samples up to one inch in diameter, and can heat a substrate to temperatures of about 600°C. Heating is via quartz halogen lamps. The dispersal ring and sample holder are isolated from the chamber walls using insulated feed throughs. This allows for bias voltages to be applied to these two structures. Note that the dispersal ring has a mesh (1 mm) screen covering it. When the system is in operation the plasma glow from the RF excitation is contained within the tube leading into the main system, and bias voltages are applied that minimize current flow between the gas dispersal ring and ground, and between the substrate holder and ground. The exact value of bias applied

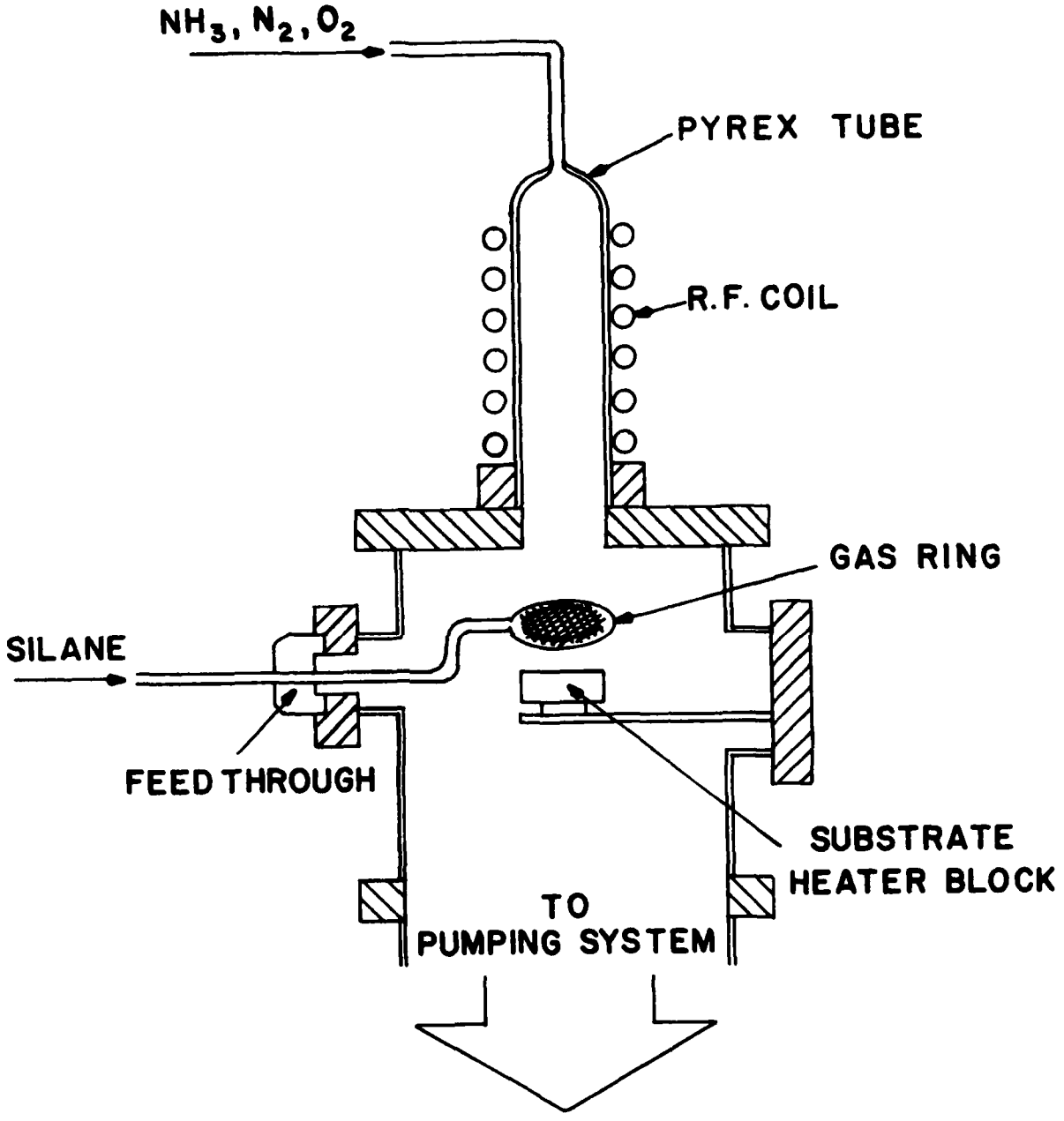

Figure 2 - Schematic Representation of Deposition Chamber

TABLE I: Deposition parameters for optimized Si_3N_4 and SiO_2 layers

Sample	Flow Rates (sccm)			Gas Ratios		Rate
	SiH_4	O_2	NH_3	O_2/SiH_4	NH_3/SiH_4	(A/Sec)
Nitride	6.5	---	75.0	---	112	0.25
Oxide	6.4	79.4	---	48.1	---	1.10

All depositions done at a pressure of 0.32 Torr, and with a power of 8.0 watts delivered to the excitation region of the upper gas feed tube.

depends on the gas flow conditions, and the particular deposition.

e. The Control System

The overall operation of the system can be either manually or computer controlled. The system is constructed with safety in mind, and in order for the system to operate, all safety subsystems must be operative. These include the blower on the exhaust system, the scrubber and the process pumps. In the computer controlled mode, the process is totally automated. This includes all gas introductions, substrate heating, etc.

2. The Deposition Process Chemistry

The process chemistry is based on the generation of specific gas phase precursor molecules, which under CVD reactions to yield the desired thin films. We have developed a model for the deposition process that is based on the chemistry of static DC silane discharges as studied by Longeway et al. [3].

a. Static DC Discharges

Static DC discharges of SiH_4 have been shown to follow a sequence of reactions that can be described as taking place in three distinct phases:

PHASE I: The Generation of Chemically Active Radical Species

The primary active species generated initially in SiH_4 discharges are the SiH_3 radical and the SiH_2 molecule. These aregenerated via interactions between energetic electrons and the SiH_4 molecules by a reaction of the type shown below:

$$SiH_4 + e^* \text{----->} SiH_3 + H_2$$

Other species can also be generated by similar reactions with excited electrons. Some of the other species created include SiH_3 and SiH_2 ions. However, by far the most important species are neutral SiH_3 radicals and SiH_2 molecules.

PHASE II: The Generation of Disilane and Trisilane Molecules

These molecules are generated by reactions between the SiH_2 molecules and the SiH_4 molecules. Typical reactions are:

$$SiH_2 + SiH_4 \text{ -----> } Si_2H_6, \text{ and}$$

$$SiH_3 + Si_2H_6 \text{ -----> } Si_3H_8 + H_2.$$

These species that undergo further reactions in which the molecular weight of silane polymer constituents is increased.

PHASE III: The Generation of Polysilane Powders

Attachment reactions of the types shown above continue with the eventual formation of polysilane species. These will then condense as powders, typically brown, red orange or yellow solids. These polysilanes have been characterized as polymer species of the general forms $(SiH_2)_N$ and $(SiH)_N$.

If we deliver an excited rare gas species through the top of our reaction chamber, and have it interact with neutral SiH_4, we then generate polysilane powders in the gas manifold of our system below the substrate holder. We interpret this experiment in the following way. Electrons created during the excitation of the rare gas species interact with the SiH_4 at the dispersal ring. Since we are operating in a gas flow regime and pressure range, wherein the mean free path for collisions is very much smaller than the distance between the gas dispersal ring and the substrate, gaseous species, SiH_4 molecules, SiH_3 radicals, etc undergo a number of collisions and reactions before they get near the heated substrate. These collisions generate higher silane species which do not yield solid films at the heated substrate (typically 150 to 300^{o}C). Instead reactions continue until the polymer length becomes long enough to condense out the polysilane powder species discussed above. On the other hand, by introducing a reactive oxygen or nitrogen species through the top of the chamber, we can stop the sequence of silane reactions discussed above and generate precursors for the deposition of oxide or nitride films.

Longeway et al. [3] demonstrated that thin films of an a-Si:O:H alloy could be deposited by adding NO gas to the static DC SiH_4 discharge. Using mass spectrometry, they showed that the active

precursor species for the solid state film was disiloxane, $(SiH_3)_2$-O, and that the other reaction product was N_2O. We have used similar types of reactions to stop the silane sequence and have been successful in depositing thin films of stoichiometric Si_3N_4 and SiO_2.

b. Deposition of Si_3N_4

We have deposited thin films of stoichiometric Si_3N_4 by either of two reactions:

$(NH_3)^* + SiH_4 \text{ -----> } Si_3N_4$, or

$(N_2)^* + SiH_4 \text{ -----> } Si_3N_4$.

Both types of films are oxygen free and show no SiH IR bands (detection limit 0.5 atomic percent). However the films do show IR absorption due to NH bonds. In our model that are two gas phase precursors generated by reactions between the excited nitrogen species and the SiH_4 or silane derivatives SiH_3 or Si_2H_6. These are trisylamine, $(SiH_3)_3$-N and silozane, $(SiH_3)_2$-NH. These species must be generated in the immediate vicinity of the gas dispersal ring. The addition of the excited nitrogen species, completely eliminates any deposition of polysilane powders any where in the chamber. This is taken as evidence for a termination of the silane sequence and the generation of precursor for Si_3N_4 depositions. We believe that the deposition of stoichiometric films requires a surface interaction with excited nitrogen species to complete the reaction sequence. This point will be tested in a new reaction/analysis chamber that is currently under construction in our laboratory.

c. Deposition of SiO_2

We have deposited thin films of SiO_2 by the reaction:

$(O_2,He)^* + SiH_4 \text{ ----> } SiO_2$.

We believe that the gas phase precursor in this case is disiloxane, $(SiH_3)_2$-O, and that a surface reaction is necessary to complete the reaction. We have not identified a specific role for the excited He gas.

d. Other Comments on Reaction Chemistry

We noted earlier that most other PECVD deposition schemes for generating SiO_2 utilized N_2O, rather than O_2 as the source of oxygen. This derives from the requirement of simultaneous excitation of all gas phase species in a capacitively coupled system. Mixing of neutral SiH_4 and O_2 results in a spontaneous reaction in which particulate SiO_2 is generated. Therefore the use of O_2 in capacitively coupled systems is not possible. In our system we use this reaction to advantage as a leak detector for O_2 (and also H_2O). Any leakage of O_2 (or H_2O) into our reaction chamber will result in spontaneous reaction with the SiH_4 gas at the dispersal ring. This in turn will generate a white powder that is easily detected directly, or through pin hole generation in the deposited films. This in effect means that the only way that oxygen impurities can be brought into our nitride films is with the excited gas species, either N_2 or NH_3. We have used high purity reagents to minimized this source of contamination.

3. Characterization of Deposited Films

We have characterized the chemical properties of the deposited films by a vareity of techniques including: (a) infra red (IR) absoprtion spectroscopy; Auger Electron Spectroscopy (AES); (c) X-Ray Photoelectron Spectroscopy (XPS); and (d) Rutherford Back Scattering (RBS). Our interest in these techniques is two fold: (1) to gives us a way of determining the stoichiometric ratios of Si to N for Si_3N_4, and Si to O for SiO_2; and (2) to identify the impurity atoms or native defect bonding arrangements. These spectroscopies all have sensitivities in the 0.X to 1.0 atomic percent range. We have not attempted to analyze the films by other techniques, for example Secondary Ion Mass Spectrometry (SIMS) which is inherently more sensitive and therefore useful for the determination of low level impurities (in the one to one thousand part per million range).

We have used all four spectroscopies mentioned above to determine the ratio of constituent atoms or the degree of stoichiometry. Consider first IR, which in addition gives us information

relative to other types of local bonding groups. Fig. 3 gives the IR absorption for stoichiometric Si_3N_4 and SiO_2, and for a Si-rich a-Si:N:H alloy film. We have used the frequency of the Si-N stretching vibration near 870cm^{-1} to determine the stoichiometry. Fig. 4 gives a plot of this frequency as a function of some of the deposition variables. This frequency goes through a maximum value at the stoichiometric Si/N ratio. We have confirmed this using information from the other three spectroscopies, i.e., AES, RBS and XPS. In addition the IR spectrum of the stoichiometric Si_3N_4 indicates the incorporation of a small fraction of NH groups. These are present in deposited films for both sources of nitrogen atoms, NH_3 or N_2. We believe that they derive from the gas phase precursor silozane, which is isoelectronic with disiloxane. The IR spectrum indicates the absense of SiH bonding groups, i.e., there is no measureable absorption near 2150cm^{-1}. Note that this band is present in the a-Si:N:H alloy film. Similar considerations apply to SiO_2. The IR spectrum indicates no measureable concentration of SiH groups (no absorption near 2250cm^{-1}), and only very weak absorption near 3600cm^{-1}, the characteristic vibrational frequency of OH bonding groups. We take the very low concentration of OH groups to be indicative of the inherent instability of silicon alcohol species of the form $HO-SiH_3$. These alcohols, if generated at all, generally are expected to react with one another and produce disiloxane. As in the case of Si_3N_4, the frequency, and in this case general shape of the Si-O stretching vibration near 1050cm^{-1} can be correlated with the stoichiometric Si/O ratio. Table I lists the deposition conditions used to obtain stoichiometric Si_3N_4 and SiO_2 in our system.

4. Device Fabrication and Performance

In collaboration with the group st RTI, we have fabricated three different types of IGFET devices using dielectric films of Si_3N_4 and SiO_2 prepared by the RPECVD process described above. In each instance the insulating film was deposited on a p-type (In,Ga)As layer that had been growm by liquid phase epitaxy on an InP substrate. Source and drain contacts were ion-implanted, and any

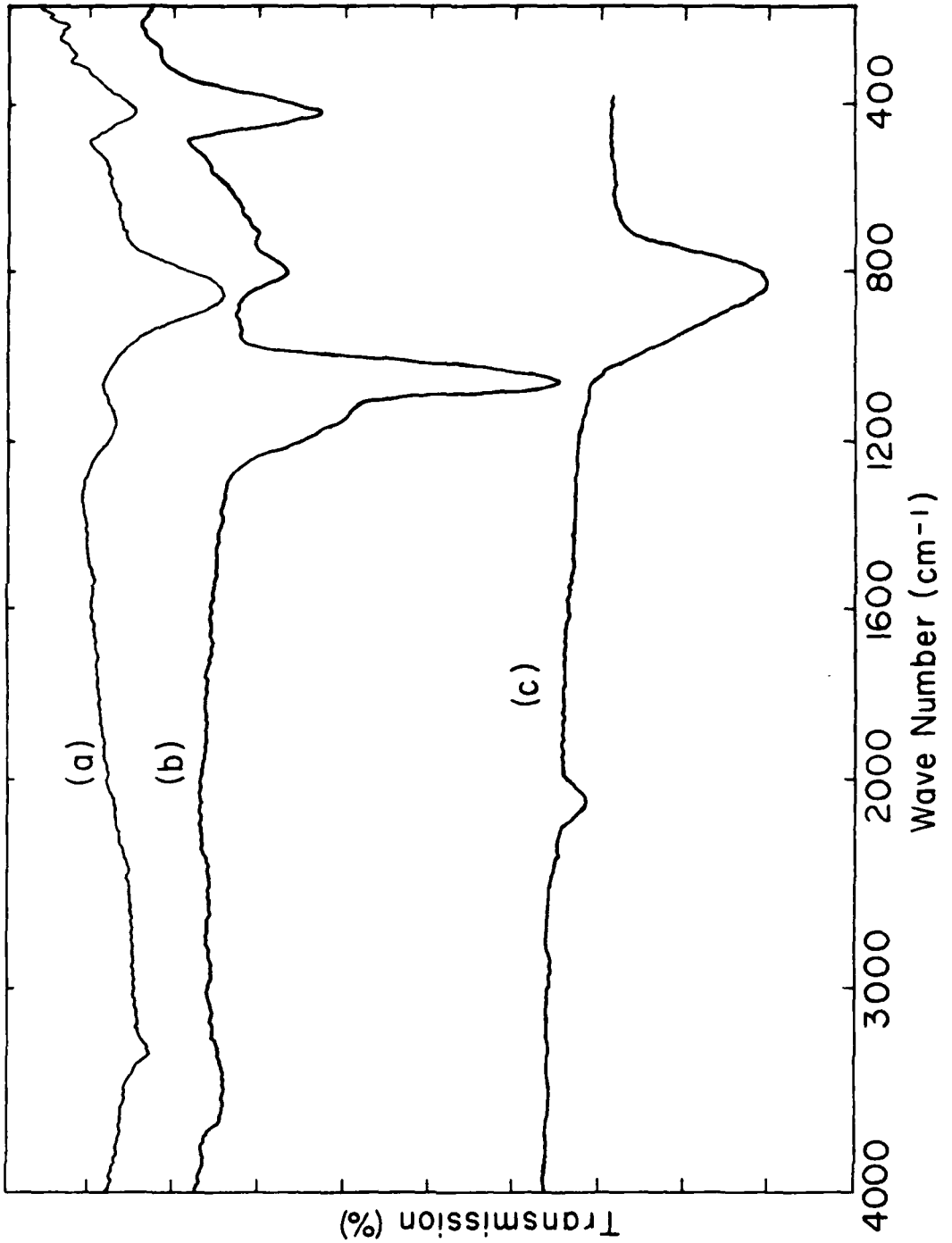

Figure 3 - IR Absorption Spectra of Si3N4, SiO2 and an a-Si:N:H Alloy

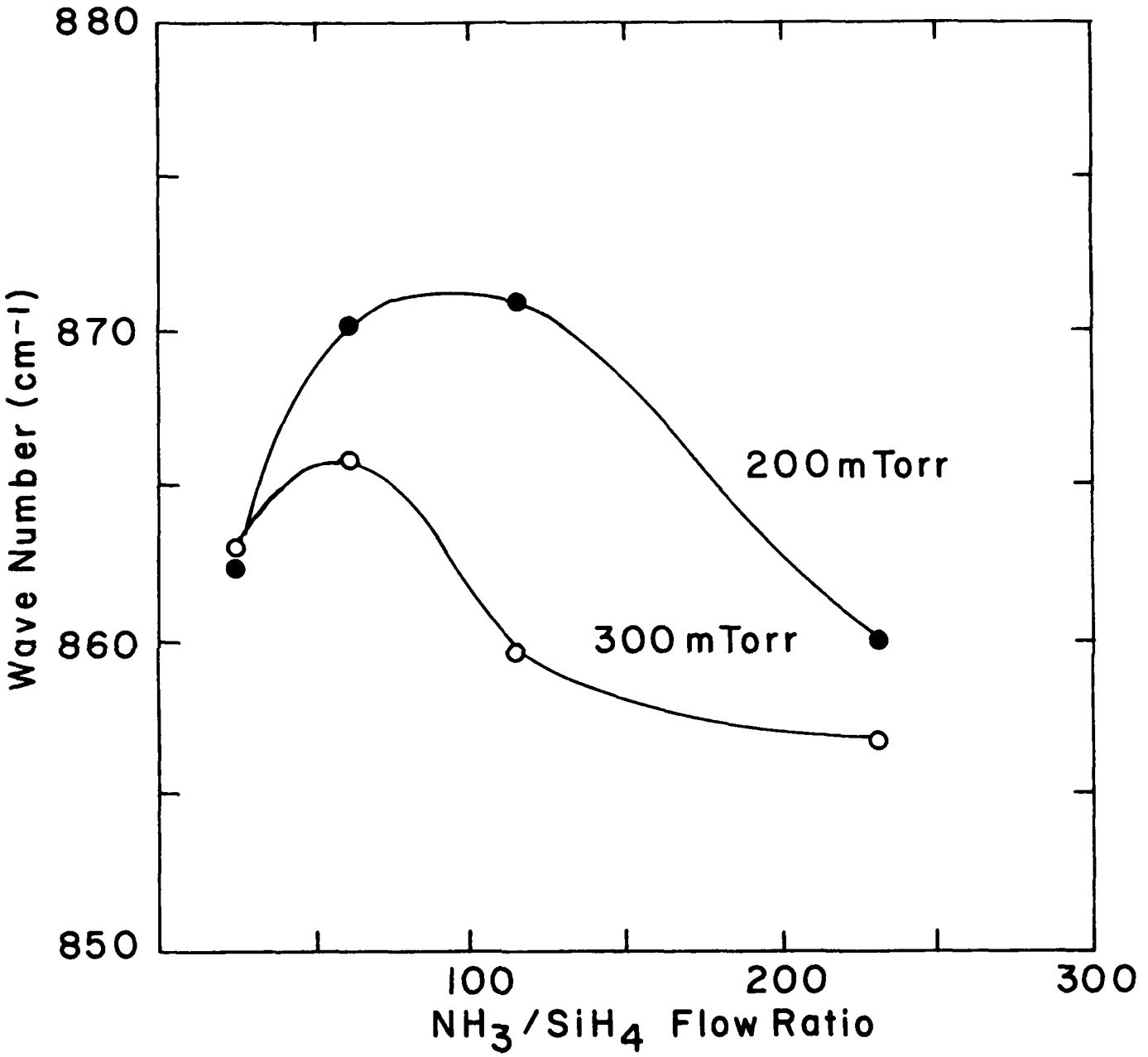

Figure 4 - Viriation of Si-N Stretching Frequency as a Function of Deposition Variables

annealing necessary to activate the carriers in these contact regions, and/or to remove radiation damage from the implantation step was done prior to the insulator depositions. The first two types of devices were fabricated with single layer dielectrics of either Si_3N_4 or SiO_2. Device performance is summarized in Fig. 5.

Devices fabricted with Si_3N_4 layers displayed low values of the transconductance, typically 2 mS/mm, but were relatively stable under long term DC bias (24 hour test period). The low value of the transconductance was correlated with electron tunnelling into the dielectric film, and subsequent deep trapping of the injected electrons. This is consistent with the observation that Si_3N_4 films can not in general be grown without relatively high concentrations of native bonding defects, presumably either Si dangling bond defects, or Si-Si bonds [4]. In contrast, devices fabricated with SiO_2 dielectric layers, showed significantly higher values of transconductance, about 30 mS/mm, but with considerable drift (about fifty percent) under prolonged DC bias. We attribute this drift to Ga diffusion through the SiO_2 layer. We have tried a third approach based on a trilayer dielectric sandwich.

The trilayer dielectric consists of a 600 A Si_3N_4 layer sandwiched between two 100 A SiO_2 layers. Our presumptions are: (1) that the SiO_2 layers act as tunnel injection barriers and eliminate injection of electrons in the Si_3N_4 layer from both the semiconductor layer and the gate electrode; and (2) that the Si_3N_4 layer acts as a diffusion barrier to ionic currents. The best devices displayed n-channel conductivity, i.e., inversion of the p-type conductivity of the as grown (In,Ga)As layer, and values of the transconductance ranging from 50 mS/mm to 75 mS/mm. The values of 50 mS/mm were on devices wherein the (In,Ga)As layer was not subjected to an in situ NH_3 plasma etch, and the values of 75 mS/mm were for devices subjected to an in situ NH_3 plasma etch. We believe that the etch helped to remove any residual native oxides. In both cases, the devices with the trilayer structure displayed excellent stability under prolonged DC bias.

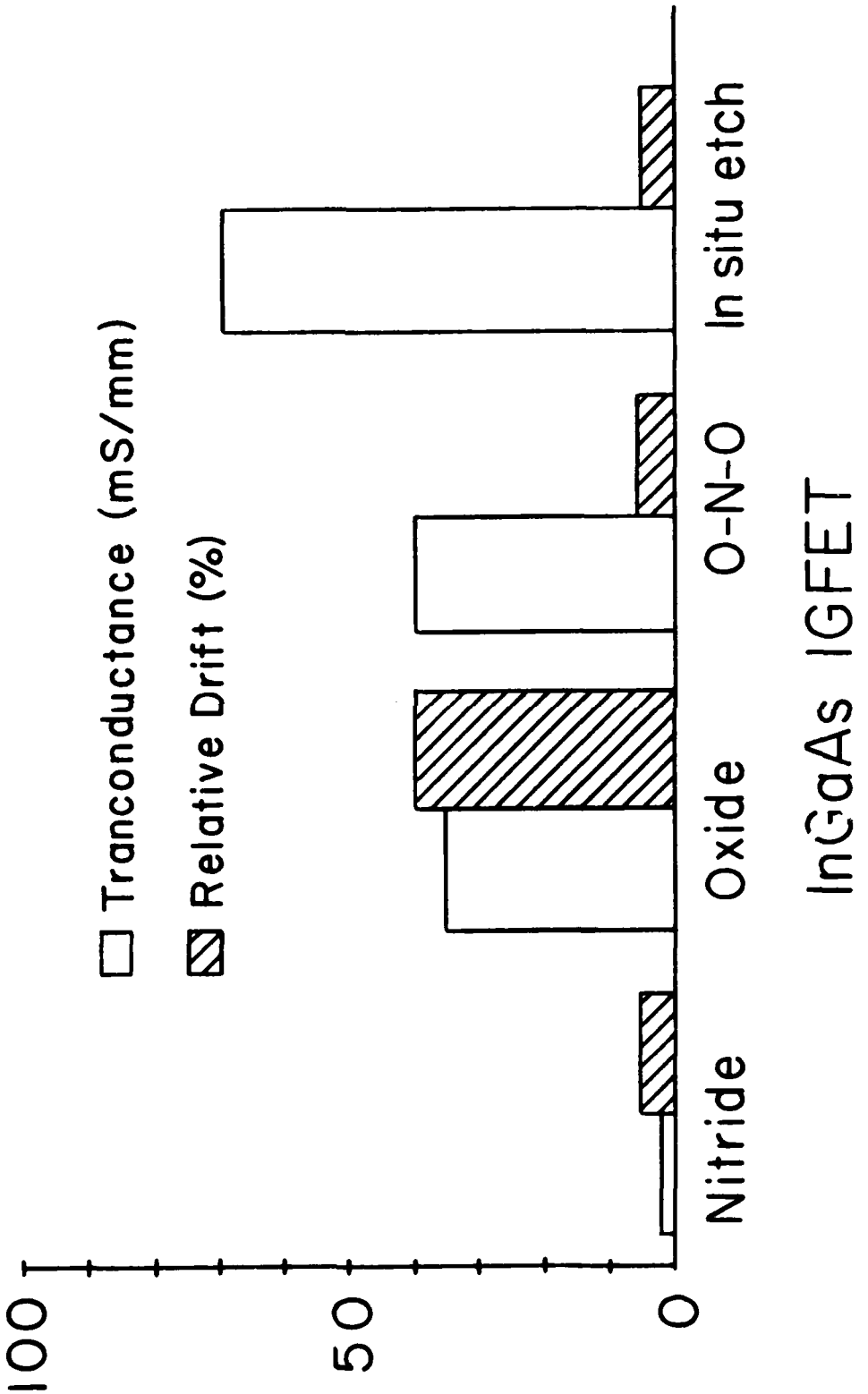

Figure 5 - (In, Ga)As IGFET Performance

5. Theory

There are two aspects of theory in which we have made significant contributrions. These are: (1) the theory of the vibrational properties of glasses, and (2) the theory of the electonic properties of bonding defects in non-crystalline solids. In each instance, the work was done under joint sponsorship with ONR under contract N00014-79-C-0133.

a. Theory of the Vibrational Properties of Glasses

This work was aimed specifically at the vibrational properties of oxide and chalcogenide glasses, and at explaining features in three complementary spectra, the IR absorption, the Raman scattering and the vibrational density of states, as revealed in X-ray scattering. In order to do this a theory must include realistic descriptions of the short and intermediate range atomic order (the SRO and IRO respectively), and good parameters, in the form of short range force constants, and IR and Raman matrix elements. We have developed a refinement of the Bethe Lattice Method that allows us to associate dominant features in each of the three spectra with specific aspects of the SRO and IRO.

We will not present a detailed description of the theory, but instead will point out that this work is included in one of the papers mentioned in the appendix: "Vibrational Properties of Glasses: Intermediate Range Order", by G Lucovsky, C.K. Wong and W.B. Pollard, J Non-Cryst Solids 59 & 60, 839 (1983). The paper includes specific calculations for As_2O_3, As_2S_3, GeO_2 and $GeSe_2$. The IR spectra of As_2O_3 and As_2S_3 are compared with the specific purpose of identifying the increased IRO in As_2O_3 in the form of six-membered rings of bonded atoms. A similar comparsion between GeO_2 and $GeSe_2$ reveals ring associated features in $GeSe_2$. Other aspects of these comparisons highlight aspects of the SRO and the mass differences between O and S, and O and Se and their effect on the spectra.

2. Native Bonding Defects in Si_3N_4 and SiO_2

This work agains draws on the Bethe Lattice method of characterizing the structure of disordered solids. We have shown in earlier papers, those by Lin, Lucovsky and Pollard, and Lucovsky and Lin included in the appendix, that the energies of Si atom dangling bond defects can be shifted appreciably by near neighbor alloy or impurity atoms. We have studied a similar problem in Si_3N_4 and SiO_2 where the particular native bonding defects were Si atom dangling bonds and Si-Si bonds. We have calculated the energies of these defect states in chemically pure Si_3N_4 and SiO_2, and in Si_3N_4 containing O and SiO_2 containing N. This study was motivated by the fact that nitrides and oxides produced by PECVD in capacitively coupled systems frequently contain chemical impurities in the form of O in Si_3N_4 and N in SiO_2. The results of our calculations are included in the paper "Near Neighbor Chemical Bonding Effects on Si-Atom Native Bonding Defects in Silicon Nitride and Silicon Dioxide Insulators", by S.Y. Lin and G Lucovsky, J Vac Sci Tech B (in press).

The major results of this paper are two: (1) that Si atom dangling bond defects and Si-Si bonding defects in Si_3N_4 and Si_3N_4:O are at essentially the same energies; i.e., the dangling bond states near the conduction band edge, and the Si-Si dates near mid-gap are not perturbed by the substitution of near neighbor O atoms in the Si_3N_4 network: and (2) in constrast, the energies of both Si dangling bond states and Si-Si states in SiO_2 relative to those in SiO_2:N are shifted downward in energy by the substitution of near neighbor nitrogen atoms for oxygen atoms.

E. SUMMARY AND RECOMMENDATIONS

1. SUMMARY

Experimental Studies

a. Deposition of Insulating Films

We have developed and refined a new process for the deposition of high quality insulating thin films of silicon nitride and silicon oxide by the technique of Remote Plasma Enhanced CVD. The key features of the process and equipment are (1) the design of the apparatus, and in particular the cleanliness of the high vacuum environment prior to deposition, and (2) the control over the gas phase and surface chemistry that is inherent in remote, and selective excitation of the gas phase reactants. The films of Si_3N_4 and SiO_2 that we have produced are qualitatively different than those produced by other PECVD techniques. Specifically our films contain no detectable Si-H groups in either the nitride or the oxide, and no detectable oxygen impurities in the Si_3N_4 or nitrogen impurities in the SiO_2. We believe that these differences in local bonding character play a significant role in the performance of the deposited films in gate insulator applications.

b. Fabrication of (In,Ga)As IGFET's

We have shown, in collaboration with the group at RTI, that it is possible to fabricate high gain (75 mS/mm), stable (less than five percent drift under 24 hour DC bias) Field Effect Transistors on (In,Ga)As. This was accomplished using as trilayer dielectric sandwich consisting of SiO_2 (100 A)-Si_3N_4 (600 A)-SiO_2 (100 A). The devices are fabricated on p-type material, and in the on mode the channel layer conduction is by electrons, so that band inversion is achieved. This indicates that the density of defects on the p-type (In,Ga)As surface, after the in situ etch and insulator deposition is sufficiently low to allow for inversion, and good transistor action with long term DC bias stability.

Theoretical Studies

These studies were done with joint support from ONR, under contract N00014-79-C-0133. A common theme in all of the theoretical work has been the introduction of structural models based on realistic bonding chemistry. Many theoretical studies of the properties of non-crystalline solids neglect this important aspect of the atomic structure, and use structural models which are inherently defecient. We have had great success in taking the alternative course of building the chemistry into the structural models. The two studies, discussed above rely heavily on aspects of bonding chemistry, and give results in close agreement with experiment in all cases where such comparisions are possible.

(2) RECOMMENDATIONS

We recommend that the experimental work started under this contract be continued. There are a number of specific applications for deposited dielectrics that are worth looking into, and a number of logical extensions of the method that may open up new opportunities in other materials systems. We therefore recommend:

1. A study of the use of trilayer dielectrics on other compound semiconductors, including GaAs, InP and (Hg,Cd)Te.
2. A study of the use of trilayer dielectrics as passivation layers on other devices, such as photodiodes, MESFETS, etc.
3. A more detailed study of the reaction chemistry involved in RPECVD deposition. This technique should work for other materials systems. We have designed an analysis/deposition system that we believe can perform this general task, and permit deposition as well. We would welcome the opportunity to submit a proposal on this system and its applications to semiconductor device technology.

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APPENDIX

We have included with this final report, abstracts of five publications that give technical details relevant to the main points discussed in the body of the report.

PAPER 1: "Remote Plasma Enhaced CVD Deposition of Silicon Nitride and Silicon Oxide for Gate Insulators in (In,Ga)As FET Devices", presented at AVS National Symposium, Reno NV, December 1984, and to be published in J Vac Sci Tech A, 1985. This papers describes the deposition system, the deposition conditions, the film properties, the prccess chemistry and the fabrication and performance of FET devices.

ABSTRACT

We have deposited silicon nitride (Si_3N_4) and silicon oxide (SiO_2) thin films using remote plasma enhanced chemical vapor deposition (RPECVD). We have characterized the chemical composition of the films by infrared absorption (IR), X-Ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Rutherford back scattering (RBS), and have studied the electrical properties in metal insulator semiconductor (MIS) device configurations. We have configured the deposition system, and adjusted the gas flow rates in order to minimize (a) O contamination in the Si_3N_4 films, and (b) OH groups in the SiO_2 films. This paper describes the deposition apparatus and the process, and presents a phenomenological model for the plasma phase and surface reactions involved. We have combined both types of insulators in a tri-layer dielectric that has been used as a gate insulator for (In,Ga)As insulated gate field effect transistors (IGFETS). We have found that the electrical properties of these devices are superior to devices utilizing single layer SiO_2 or Si_3N_4 gate insulators.

PAPER 2: "Vibrational Properties of Glasses: Intermediate Range Order", presented as an invited paper at the 10th International Conference on Amorphous and Liquid Semiconductors, Tokyo, Japan, August 1983, and published in J Non-Cryst Solids. This paper discusses the innovations of the Bethe Lattice calculations, and gives results for As_2O3, As_2S_3, GeO_2 and $GeSe_2$.

ABSTRACT

This paper discusses a breakthrough in the calculation of the vibrational properties of disordered solids. Oure approach ia a refinement of the Bethe Lattice Method incorporating aspects of intermediate range order.

PAPER 3: "Near Neighbor Chemical Bonding Effects on Si-atom Native Bonding Defects in Silicon Nitride and Silicon Dioxide Insulators", presented at PCSI 11, Phoenix AZ, January 1985, and to be published in J Vac Sci Tech B, 1985. This paper presents a theoretical treatment of Si atom dangling bond and Si-Si native bonding defects based on a tight-binding method. The work builds on previous studies of Si atom dangling bonds in amorphous Si alloys.

ABSTRACT

There has been considerable interest in the use of deposited thin films of Si_3N_4 and SiO_2 as gate insulators and/or passivation layers for compound semiconductors. This is contingent on a low temperature deposition process which: (a) produces insulators which are effectively free of native bonding defects and impurity atoms; and at the same time (b) minimizes chemical degradation, and the associated generation of interfacial defect states at the compound semiconductor surfaces. Recently, the group at North Carolina State University and The Research Triangle Institute has developed a low temperature, remote plasma enhanced CVD process for depositing trilayer gate insulators consisting of SiO_2-Si_3N_4-SiO_2 layers onto p-type (In,Ga)As to produce high gain, stable, n-channel conducting FET devices. The processing chemistry prevents the incorporation of significant amounts of chemical impurities in the form of oxygen atoms in the Si_3N_4, and hydrogen and nitrogen atoms in the SiO_2. This paper addresses the question of native bonding defects in Si_3N_4 and SiO_2, and considers the effects on near neighbor impurity atoms on the gap state energies of two types of defects, Si atom dangling bonds and Si-Si bonds.

PAPER 4: "Electron Trapping States in a-Si:(H,O) and a-Si:(H,N) Alloys", published in J Non-Cryst Solids 66, 291 (1984).

ABSTRACT

The energy levels of alloy atom complexes and dangling bond defects states in a-Si host materials are determined using an empirical tight-binding formalism. These calculations demonstrate that alloy atom complexes, such as bonded-atom sequences of the forms Si-O-Si-H or Si-N-Si-H do not by themselves introduce localized states in the pseudo-gap of a-Si. However, dangling bond defects on Si atoms that are bonded to strongly electronegative atoms such as O or N produce localized states in the pseudo-gap whose energies relative to the top of the valence band are shown to vary systematically with the chemical nature of the Si neighbors. These calculations then confirm that the additional localized states in a-Si:H alloys associated with O or N impurities are dangling bonds on Si atoms which have O or N impurity atoms as their nearest neighbors.

PAPER 5: "Systematic Trends in the Energies of Dangling Bond Defect States in a-Si Alloys Containing C, N and O", published in AIP Conf Proc 120, 55 (1984).

ABSTRACT

We have used a tight-binding formalism to calculate the energies of Si-atom dangling bond defects within the pseudo-gap of a-Si alloys containing C, N and O. We have determined the energy of thge dangling bond state relative to the width of the pseudo-gap as function of the the chemical nature of the atoms that are back-bonded to the Si-atom with the dangling bond. We have considered local geometries in which all bonded neighbors are Si atomes, or where one or more of these is replaced by an alloy (or impurity) atom such as C, N or O. We find that the relative energy scales with the average electronegativity of these atoms, being near mid-gap for three Si-atoms, and about three-quarters of the way to the conduction band for two Si, and one O neighbor. We have found that this trend is independent of the way the tight-binding parameters are chosen, in particular that the inclusion of the s* state formalism of Dow and his coworkers yields the same trends as other parameterizations used by Chadi and his coworkers.

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